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STOPPED-FLOW KINETICS OF THE AMMONATION OF CIS-DICHLORODIAMMINEPALLADIUM (II)

Ross Gordon Hibler

NAVAL POSTGRADUATE SCHOOL
Monterey, California

THESIS

STOPPED-FLOW KINETICS OF THE AMMONATION
OF CIS-DICHLORODIAMMINEPALLADIUM (II)

BY

ROSS GORDON HIBLER

December 1974
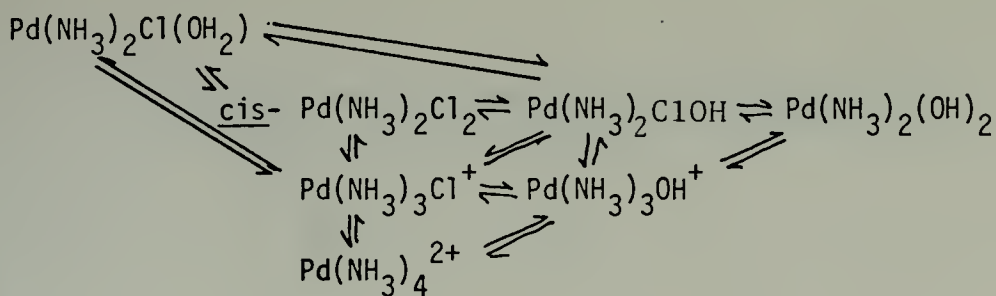
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Cis-dichlorodiamminepalladium(II) was synthesized and identified by its unique infrared spectrum. The reaction of cis-dichlorodiamminepalladium(II) with ammonia in varying concentrations of sodium chloride was studied using stopped-flow techniques. An analysis of the following system was completed and discussed in the light of experimental rate constants:

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$$Pd(NH_3)_2Cl(OH_2) \rightleftharpoons$$

$$\underline{cis}\text{-} Pd(NH_3)_2Cl_2 \rightleftharpoons Pd(NH_3)_2ClOH \rightleftharpoons Pd(NH_3)_2(OH)_2$$

$$Pd(NH_3)_3Cl^+ \rightleftharpoons Pd(NH_3)_3OH^+$$

$$Pd(NH_3)_4^{2+}$$

Anomalies arising in the experimental results were discussed and recommendations for further work were made.

Stopped-Flow Kinetics of the Ammonation of
<u>cis</u>-Dichlorodiamminepalladium(II)

by

Ross Gordon Hibler
Lieutenant Commander, United States Navy
B.S., University of Idaho, 1965

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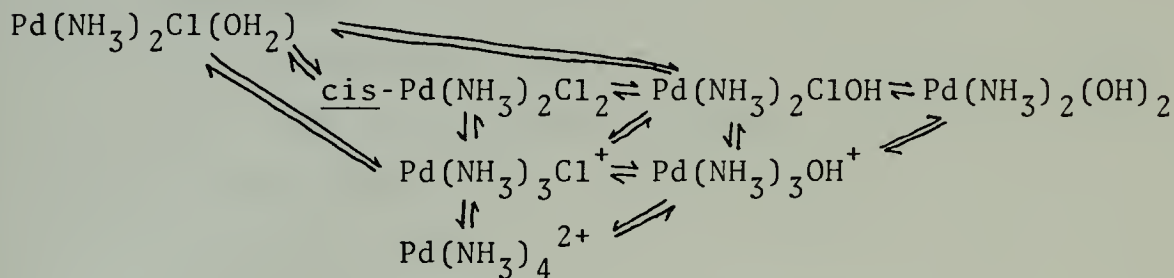requirements for the degree of

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ABSTRACT

$\underline{Cis}$-dichlorodiamminepalladium(II) was synthesized and identified by its unique infrared spectrum. The reaction of $\underline{cis}$-dichlorodiamminepalladium(II) with ammonia in varying concentrations of sodium chloride was studied using stopped-flow techniques. An analysis of the following system was completed and discussed in the light of experimental rate constants.

$$Pd(NH_3)_2Cl(OH_2)$$

$$\underline{cis}\text{-}Pd(NH_3)_2Cl_2 \rightleftharpoons Pd(NH_3)_2ClOH \rightleftharpoons Pd(NH_3)_2(OH)_2$$

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Anomalies arising in the experimental results were discussed and recommendations for further work were made.

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I.   INTRODUCTION

A study of metal ion complexes in solution yields infor-
mation useful for reaction catalysis. The kinetics of sub-
stitution reactions for these complexes is not yet understood.
The ammonia complexes of palladium, a transition metal, have
been the subject of numerous recent investigations (1,2,3,4,
5,6,7,8,9,10). With an eye to elucidating further the be-
havior of these complexes, kinetic studies involving the
substitution of ammonia on cis-dichlorodiamminepalladium(II)
were undertaken.

As is the case with nickel, the +2 oxidation state of
palladium (Pd(II)) is the more common. Pd(II) has a d^8
electronic configuration and a coordination number of four,
such that the complexes formed are square planar (11).

Substitution reactions of square-planar complexes in
aqueous solution have shown historically a two term rate law
of the form:

$$\text{Rate} = \frac{-d(\text{complex})}{dt} = \left\{ k_1 + k_2(Y) \right\}(\text{complex})$$

where k_1 is a first order rate constant, k_2 is a second order
rate constant, (Y) is the concentration of the entering
ligand in moles per liter, and (complex) is the concentration
of the complex in moles per liter (11,12). A rate law of
this form is consistent with postulation of parallel associa-
tive paths, namely:

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(1) departing ligand replacement by solvent molecule
followed by its rapid replacement by the entering ligand,
giving the first term.

(2) direct replacement of departing ligand by entering
ligand, giving the second term.

A number of authors have dealt with the problems of
elucidating the kinetics and mechanism of the various ammonia
substitution reactions of the $PdCl_4^{2-}$ ion. The basic scheme
showing significant species is:

$$PdCl_4^{2-} \rightleftharpoons Pd(NH_3)Cl_3^{-} \underset{trans\text{-}Pd(NH_3)_2Cl_2}{\overset{cis\text{-}Pd(NH_3)_2Cl_2}{\rightleftharpoons}} Pd(NH_3)_3Cl^{+} \rightleftharpoons Pd(NH_3)_4^{2+}$$
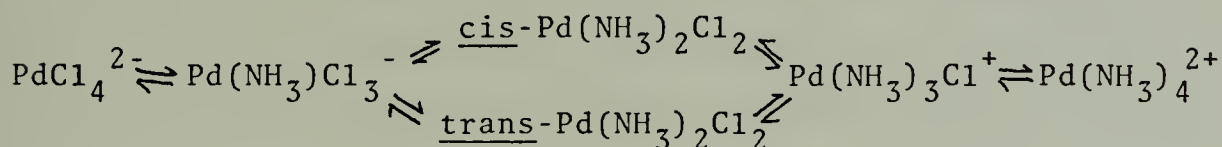
Several investigations (1,3) have focused on the reaction
of cis-dichlorodiamminepalladium(II) with ammonia and have
shown a rate law of the following form for the first and
second ammonia substitutions:

$$Rate = \frac{-d(complex)}{dt} = \left\{ k_1 \frac{(NH_3)}{(Cl^-)} + k_2(NH_3) \right\}(complex) \qquad (1)$$

where k_1 and k_2 are rate constants and (complex), (NH_3) and
(Cl^-) are the concentrations in moles per liter of indicated
species. The above form can be rationalized by postulating
for the first term a pre-equilibrium aquation, followed by
the rate-determining replacement of associated solvent ligand
by the entering ammonia. Atwill's (3) investigation showed
anomalous temperature and chloride ion variations; additionally,
his investigation was burdened with the necessity of

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maintaining relatively low (10° to 20^OC) reaction temperatures and ammonia concentrations in order to obtain measurably slow reaction rates.

The goal of this research was to study the reaction of cis-$Pd(NH_3)_2Cl_2$ with ammonia using stopped-flow techniques. This method would allow measurement of relatively large rate constants; thus, ammonia concentrations up to 0.25M could be utilized, which represents a 500-fold increase over the concentrations permitted by classical kinetic techniques. Straightforward pseudo-first order kinetics were expected due to this increased ammonia concentration, as well as the ability to conduct kinetic studies at temperatures well above 25^OC.

II. EXPERIMENTAL

A. MATERIALS

Reagent grade materials were used throughout the study without further purifucation, the only exception being the cis-Pd(NH$_3$)$_2$Cl$_2$ which was prepared locally by the method of Coe and Lyons (13) as modified by Atwill (3).

B. ANALYSIS OF SYNTHESIZED Pd(NH$_3$)$_2$Cl$_2$

The synthesized product was concluded to be cis-Pd(NH$_3$)$_2$Cl$_2$ on the basis of the following results:

1. Chemical Test

An initial qualitative examination of the synthesized cis-Pd(NH$_3$)$_2$Cl$_2$ was conducted by observation of the rapidity of appearance of a red-brown color when small amounts of materials being examined were added to test tubes containing a saturated solution of potassium iodide in acetone (14). Observations are listed in Table I.

TABLE I

Substrate	Time (minutes)	Observation
Commercial trans-Pd(NH$_3$)$_2$Cl$_2$[1]	5+	transparent orange
Local cis-Pd(NH$_3$)$_2$Cl$_2$ (A)[2]	0.5	opaque red-brown
Local cis-Pd(NH$_3$)$_2$Cl$_2$ (B)[2]	0.5	opaque red-brown
Aged cis-Pd(NH$_3$)$_2$Cl$_2$ from laboratory of Dr. Reinhardt[2]	0.75	opaque red-brown

---

[1] Research Organic Chemical Company, lot number Pd-14

[2] (A) and (B) samples were from initial and final precipitations, respectively, in local synthesis.

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2. Infrared Analysis

An infrared absorption spectrum through a KBr pellet was obtained using a Perkin-Elmer 621 infrared spectrophotometer (features double beam and multiple gratings as well as extended range) where the doublet in the Pd-N stretching region (495-476 cm^{-1}) as well as other characteristic $\underline{cis}$-Pd(NH$_3$)$_2$Cl$_2$ features (15) were noted.

3. Ultraviolet Spectrum

To eliminate the possibility of significant amounts of non-palladium impurities, such as glass from glass filters, a quantitatively prepared solution of $10^{-3}\underline{M}$ $\underline{cis}$-Pd(NH$_3$)$_2$Cl$_2$ was filtered and then converted to PdCl$_4$$^{2-}$ with excess HCl. Its spectrum in 1.0$\underline{M}$ NaCl was obtained utilizing the Beckman DK-1A recording spectrophotometer with 1.0$\underline{M}$ NaCl as reference. The features of this spectrum as well as absorbances were compared to Cohen and Davidson's results (16). Quantitative interpretation of the spectrum indicated the absence of significant masses of non-palladium contaminants.

C. EQUIPMENT

1. Stopped-Flow Apparatus

The basic stopped-flow apparatus (hereafter, SFA), (figure 1), was designed by Kenneth J. Graham, Chemist, NPS, and constructed by NPS research machinist Donald Harvey. Lucite (polymethylmethacrylate) was chosen to construct the SFA body due to its low thermal conductivity and easy machinability. All valves were fabricated from Teflon. Detectable spurious light was eliminated by painting the

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Figure 1. Block Diagram of Stopped-Flow System.

Block Diagram Showing Location
of Lamp Housing

Block Diagram of Temperature
Control System

Figure 2.

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SFA body flat black. Temperature control was achieved by circulation of water from a thermostatted bath through a split system of four Beckman DU thermospacers (figure 2).

The SFA mixing chamber was patterned after the design of Gibson[3], which gives 98% mixing in less than two milliseconds.[4]

Precise temperature control proved to be more troublesome than anticipated. The DU lamp housing was located (figure 2) approximately 1/3 inch from the SFA body, causing a temperature gradient in the body despite intervening insulation. Judicious location of thermospacers and adjustment of bath temperature was sufficient to reduce the temperature differential between storage cells to less than $0.5^{\circ}C$. The average cell temperature differential was $0.25^{\circ}C$. Relocation of the lamp to a remote position and installation of integral temperature control should be sufficient to eliminate this problem in future investigations utilizing the SFA.

2. Data Recording and Display

An RCA 7102 photomultiplier tube (S-1 response) was utilized as the photodetector. Bandwidth ranged from 20 to 100 Hz and was varied by an RC filter (figure 1). Data for the expected slower reactions (1.0M NaCl) was recorded on a Mosely 7100B strip chart recorder which featured chart speeds of 1 in/hr to 2 in/sec and a ten inch chart width which was fully

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[3]Ref. 17, p. 121.

[4]Durrum Instrument Corp., Bulletin 131, page 14.

utilized. The expected faster reactions (0.1$\underline{M}$ NaCl) were recorded by photographing the trace of a Tectronix 434 storage oscilloscope with a Polaroid CR-9 camera.

D. KINETIC RUNS

The reaction of $\underline{cis}$-Pd(NH$_3$)$_2$Cl$_2$ with ammonia were observed by following the change in absorbance with time at a wavelength of 380 nm. All reactions were conducted at an ionic strength of 1.0 at 25°C. In each reaction the SFA mixed equal volumes of 1 x 10^{-3}$\underline{M}$ $\underline{cis}$-Pd(NH$_3$)$_2$Cl$_2$ with the chosen concentration of ammonia. When chloride ion was varied, requisite amounts of sodium perchlorate were utilized to maintain ionic strength. All solutions were filtered prior to use.

Following mixing in the SFA, the initial concentrations examined were:

(1) 5x10^{-4}$\underline{M}$ $\underline{cis}$-Pd(NH$_3$)$_2$Cl$_2$; 1.0$\underline{M}$ NaCl; 0.25,0.125,0.05$\underline{M}$ NH$_3$.

(2) 5x10^{-4}$\underline{M}$ $\underline{cis}$-Pd(NH$_3$)$_2$Cl$_2$; 0.1$\underline{M}$ NaCl; 0.25,0.125,0.05,0.025$\underline{M}$ NH$_3$.

(3) 5x10^{-4}$\underline{M}$ $\underline{cis}$-Pd(NH$_3$)$_2$Cl$_2$; 0.125$\underline{M}$ NH$_3$; 0.75,0.625,0.5$\underline{M}$ NaCl.

E. ANALYSIS SCHEME

A slow and fast observed rate constant were determined for each analyzed trace in the following manner. The transmittance at each time increment was converted to absorbance (A). The estimated absorbance at infinite time (A$_\infty$) was then subtracted and the remainder (A - A$_\infty$) plotted against time on semi-log graph paper.

Typical Trace

0

Transmittance
(%)

100

Time

Typical Plot

$\ln(A - A_\infty)$

t_2 t_1

Time

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The slope of the linear portion of the plot is
established as the observed slow step rate constant.

$$k_{obs} = \frac{\ln \frac{(A - A_\infty)_{t1}}{(A - A_\infty)_{t2}}}{t_1 - t_2}$$

The observed rate constant for the fast step was next calcu-
lated by extrapolating the linear portion of the slow step
$(A - A_\infty)$ vs time plot towards zero time and subtracting from
$(A - A_\infty)$. The remainder was then plotted against time on
semi-log graph paper and the fast step observed rate constant
computed in the same manner as for the slow step.

For each variation of parameters several traces were
analyzed. The median values of the observed rate constants
were used in the following interpretation and analysis.

F. HYDROXIDE ION SUBSTITUTION OF cis-Pd(NH$_3$)$_2$Cl$_2$

An auxilliary experiment was performed to test for the
presence of either Pd(NH$_3$)$_2$ClOH or Pd(NH$_3$)$_2$(OH)$_2$ when
hydroxide ion at a concentration of 10^{-3}M is allowed to
react with cis-Pd(NH$_3$)$_2$Cl$_2$. A one cm pathlength cuvette
was filled with 10^{-3}M cis-Pd(NH$_3$)$_2$Cl$_2$ in 0.1M NaCl and 0.9M
NaClO$_4$ and placed in the Beckman DK-1A. One drop of 0.1M
NaOH was added (giving a hydroxide ion concentration approx-
imating that in the basic SFA study) and mixed in situ. The
reaction was followed by recording percent transmission at
a wavelength of 350 nm. Two distinct reactions were observed.
The first proceeded to apparent completion within ten seconds

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and the second slower reaction did not reach completion in one hour. A possible interpretation of the faster reaction is the single and/or double hydroxide ion replacement of chloride ion in cis-$Pd(NH_3)_2Cl_2$; the nature of the slower reaction is undetermined (perhaps dimerization or olation of cis-$Pd(NH_3)_2Cl_2$).

III. RESULTS

Slow and fast observed rate constants are tabulated in Table II along with their pertinent parameters. Figures 3 through 8 show observed rate constant dependencies on ammonia and chloride ion concentrations. The observed rate constants for the slow step are seen to be proportional to $(NH_3)^{3/2}$ in both 1.0$\underline{M}$ and 0.1$\underline{M}$ NaCl and those for the fast step to $(NH_3)^{1/2}$ in 0.1$\underline{M}$ NaCl and $(NH_3)^2$ in 1.0$\underline{M}$ NaCl. For both slow and fast steps, rate constants are proportional to $(Cl^-)^{-1}$ for chloride ion concentrations between 1.0$\underline{M}$ and 0.5$\underline{M}$ in 0.125$\underline{M}$ ammonia. The data points for 0.1$\underline{M}$ NaCl are not plotted on figures 8 and 9 due to their inconsistency with the remainder of the data and the desirability of presenting the data points utilizing an expanded scale.

TABLE II

(NH_3) $\underline{M}$	(Cl^-) $\underline{M}$	Recording Device	Number of Traces	Temp. ($^\circ$C)	Observed rate constants k_{slow} (sec^{-1})	k_{fast}
0.125	0.1	Tectronix	5	24.5	0.34	7.0
0.125	0.5 [5]	Tectronix	4	24.1	0.92	8.8
0.125	0.625[5]	Tectronix	6	24.4	0.49	7.0
0.125	0.75 [5]	Mosely	3	25.3	0.60	3.4
0.125	1.0	Mosely	3	24	0.17	0.80
0.05	1.0	Mosely	6	24	0.04	0.39
0.25	1.0	Mosely	3	24	0.49	4.2
0.05	0.1	Tectronix	5	25.2	0.22	5.0
0.25	0.1	Tectronix	5	25.5	0.72	9.8
0.025	0.1	Tectronix	2	25.1	0.15	3.5

[5]Chloride ion concentrations reported in these instances differed prior to mixing, with the average value being reported.

[5](continued). Prior to mixing the chloride ion concentration in the _cis_-$Pd(NH_3)_2Cl_2$ storage cell was $1.0\underline{M}$ with the chloride ion concentration in the ammonia storage cell being varied to produce the desired average.

Figure 3. Fast Step Observed Rate Constants, k_{fast} vs. $(NH_3)^2$. Reaction temperature, $24^{\circ}C$; NaCl concentration, $1.0\underline{M}$.

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Figure 4.   Fast step observed rate constants, k_{fast} vs. $(NH_3)^{\frac{1}{2}}$.
Reaction temperature, $25^\circ C$; NaCl concentration, $0.1\underline{M}$.

Figure 5. Slow step observed rate constants, k_{slow} $\underline{vs.}$ $(NH_3)^{3/2}$. Reaction temperature, $25^{\circ}C$; NaCl concentration, $0.1\underline{M}$.

Figure 6. Slow step observed rate constants, k_{slow} $\underline{vs.}$ $(NH_3)^{3/2}$.
Reaction temperature, $24^{o}C$; NaCl concentration, $1.0\underline{M}$.

Figure 7. Slow step observed rate constants, k_{slow} vs. $1/(Cl^-)$.
Reaction temperature, 25^oC; Ammonia concentration, $0.125\underline{M}$.

Figure 8. Fast step observed rate constants, k_{fast} vs. $1/(Cl^-)$. Reaction temperature, 25^oC; Ammonia concentration, $0.125\underline{M}$.

IV. CONCLUSIONS

The experiment discussed in section II-F suggests the presence of hydroxide-substituted products. The inclusion of these species in an expanded reaction scheme can also be justified by consideration of known equilibrium constants in the chemistry of platinum, as follows:

Let $M = (Pt(NH_3)_2Cl)-$

$$MOH_2 = MOH^- + H^+ \qquad K_1 = 10^{-6}\underline{M} \quad [6] \qquad (2)$$

$$H^+ + OH^- = H_2O \qquad K_w = 10^{14} \qquad (3)$$

Summing (2) and (3):

$$MOH_2 + OH^- = MOH^- + H_2O \quad K_2 = K_1K_w = 10^{8}\underline{M}^{-1} \qquad (4)$$

$$MCl^- + H_2O = MOH_2 + Cl^- \quad K_3 = 3.3\times10^{-5}\underline{M} \quad [7] \qquad (5)$$

Summing (4) and (5):

$$MCl^- + OH^- = MOH^- + Cl^- \quad K_4 = K_2K_3 = 3.3\times10^3$$

Assigning representative chloride and hydroxide ion concentrations of $1.0\underline{M}$ and $10^{-3}\underline{M}$, respectively, leads to the following expression:

$$\frac{(MOH^-)}{(MCl^-)} = 3.3$$

---

[6]Reference (11), p.32. K_1 assigned same value as similar reaction of $Pt(NH_3)_2(OH_2)_2$. The assignment is strengthened by the observation that similar transition metal complexes (having H_2O ligands) have acid hydrolysis constants between 10^{-4} and $10^{-7}\underline{M}$.

[7]Ibid., p.357. This equilibrium constant has been estimated by Reinhardt et.al. to be on the order of $10^{-3}\underline{M}$ for the corresponding trans-palladium complex.

Thus, if the platinum analogy to palladium is valid and and the estimated value of K_3 for palladium is included in the derivation, the above ratio becomes:

$$\frac{(Pd(NH_3)_2ClOH)}{(Pd(NH_3)_2Cl_2)} = 10^2$$

and therefore the presence of hydroxide-substituted species must be considered in any proposed reaction scheme.

Such a proposed scheme is:

The above may be analyzed as follows:

Species	Symbol
$Pd(NH_3)_2Cl(OH_2)^+$	A
cis-$Pd(NH_3)_2Cl_2$	B
cis-$Pd(NH_3)_2ClOH$	C
cis-$Pd(NH_3)_2(OH)_2$	D
$Pd(NH_3)_3Cl^+$	E
$Pd(NH_3)_3OH^+$	F
$Pd(NH_3)_4^{2+}$	G

The abbreviated scheme showing equilibria and rate constants is shown below.

$$A \underset{}{\overset{K_{10}}{\rightleftharpoons}} B \underset{}{\overset{K_1}{\rightleftharpoons}} C \underset{}{\overset{K_2}{\rightleftharpoons}} D$$

$$K_{10} = \frac{(B)}{(A)(Cl^-)} \qquad\qquad K_7 = \frac{(F)(Cl^-)}{(E)(OH^-)}$$

$$K_1 = \frac{(C)(Cl^-)}{(B)(OH^-)} \qquad\qquad K_{12} = \frac{(NH_4^+)(OH^-)}{(NH_3)} = 1.8 \times 10^{-5} \underline{M}$$

$$K_2 = \frac{(D)(Cl^-)}{(C)(OH^-)}$$

If the variable S is defined as the sum of A + B + C + D, then a theoretical form for the first step rate law may be derived as follows:

$$S = A + B + C + D$$

$$= B\left\{ \frac{1}{K_{10}(Cl^-)} + 1 + \frac{K_1(OH^-)}{(Cl^-)} + \frac{K_1 K_2 (OH^-)^2}{(Cl^-)^2} \right\}$$

$$\dot{S} = k_{11}(A)(NH_3) + k_3(B)(NH_3) + (k_4+k_5)(C)(NH_3)$$

$$\quad + k_6(D)(NH_3)$$

$$\dot{S} = (B)\left\{ \frac{k_{11}(NH_3)}{K_{10}(Cl^-)} + k_3(NH_3) + \frac{(k_4+k_5)K_1(OH^-)(NH_3)}{(Cl^-)} \right.$$

$$\left. + \frac{k_6 K_1 K_2 (OH^-)^2 (NH_3)^2}{(Cl^-)^2} \right\}$$

$$(\dot{S}) = \left\{ \frac{(S)}{\dfrac{1}{K_{10}(Cl^-)} + 1 + \dfrac{K_1(OH^-)}{(Cl^-)} + \dfrac{K_1K_2(OH^-)^2}{(Cl^-)}} \right\}$$

$$\left\{ \frac{k_{11}(NH_3)}{K_{10}(Cl^-)} + k_3(NH_3) + \frac{(k_4+k_5)K_1(OH^-)(NH_3)}{(Cl^-)} + \frac{k_6K_1K_2(OH^-)^2(NH_3)^2}{(Cl^-)^2} \right\} \quad (6)$$

The interpretation of the above rate law is simplified if the dependence of hydroxide ion concentration on ammonia concentration is noted.

$$NH_3 + H_2O \underset{}{\overset{K_{12}}{\rightleftharpoons}} NH_4^+ + OH^-$$

$$K_{12} = \frac{(NH_4^+)(OH^-)}{(NH_3)} = 1.8 \times 10^{-5}\underline{M}$$

Thus, if hydroxide and ammonium ion concentrations are approximately equal and the ammonia concentration is sufficiently high, the hydroxide ion concentration will be proportional to the one-half power of the ammonia concentration. The assumption of the equivalence of hydroxide and ammonium ion concentrations will be valid only if the sum of the concentrations of the hydroxide-substituted species is much less than the sum of the concentrations of the non-hydroxide-substituted species. Now the derived rate law (6) may be written in a form where (OH⁻) has been replaced by $K_{12}^{\frac{1}{2}}(NH_3)^{\frac{1}{2}}$:

$$\dot{(S)} = \left\{ \cfrac{(S)}{\cfrac{1}{K_{10}(Cl^-)} + 1 + \cfrac{K_1 K_{12}^{1/2}(NH_3)^{1/2}}{(Cl^-)} + \cfrac{K_1 K_2 K_{12}(NH_3)}{(Cl^-)}} \right\}$$

$$\left\{ \cfrac{k_{11}(NH_3)}{K_{10}^-(Cl^-)} + k_3(NH_3) + \cfrac{(k_4 + k_5) K_1 K_{12}^{1/2}(NH_3)^{3/2}}{(Cl^-)} + \cfrac{k_6 K_1 K_2 K_{12}(NH_3)^3}{(Cl^-)^2} \right\}$$

(7)

The derived theoretical rate law for the first ammonation step (7) has sixteen possible dominant terms. The following are of interest due to their similarity to the experimentally determined ammonia and chloride dependences of the observed rate constants:

Case (1): $\dot{(S)} \propto \dfrac{(S)(NH_3)^{3/2}}{(Cl^-)}$ if in (7) 1 >> sum of

remainder of the terms in the denominator of the first bracket and the third term >> sum of remainder of the terms of the second bracket. The above restrictions correspond to cis-$Pd(NH_3)_2Cl_2$ being the dominant species in S and to either steps

$$Pd(NH_3)_2ClOH + NH_3 \longrightarrow Pd(NH_3)_3Cl^+ + Cl^-$$

or

$$Pd(NH_3)_2ClOH + NH_3 \longrightarrow Pd(NH_3)_3OH^+ + OH^-$$

as being rate-controlling (the two cases being kinetically indistinguishable).

Case (2): $(\dot{S}) \propto (S)\dfrac{(NH_3)^2}{(Cl^-)}$ if in (7) $\dfrac{1}{K_{10}(Cl^-)} \gg$ sum of

remainder of the terms in the denominator of the first

bracket and the fourth term $\gg$ sum of remainder of the

terms in the second bracket. The above restrictions

correspond to $Pd(NH_3)_2Cl(OH_2)$ being the dominant term

in S and to

$$Pd(NH_3)_2(OH)_2 + NH_3 \rightarrow Pd(NH_3)_3OH^+ + OH^-$$

being the rate-controlling step.

Case (3): $(\dot{S}) \propto (S)\dfrac{(NH_3)^{3/2}}{(Cl^-)}$ if in (7) $\dfrac{K_1K_{12}^{1/2}(NH_3)^{1/2}}{(Cl^-)}$

is $\gg$ sum of remainder of the terms in the denominator

of the first bracket and the fourth term $\gg$ sum of the

remainder of the terms of the second bracket. The above

restrictions correspond to $Pd(NH_3)_2ClOH$ being the dominant

term in S and to the step

$$Pd(NH_3)_2(OH)_2 + NH_3 \rightarrow Pd(NH_3)_3OH^+ + OH^-$$

being rate-controlling.

A theoretical form for the second ammonation step may

be developed in a similar manner. Define a variable T equal

to the sum of E and F:

$$(T) = (E) + (F) = (F)\left\{1 + \dfrac{(Cl^-)}{K_7(OH^-)}\right\}$$

$$(\dot{T}) = k_8(E)(NH_3) + k_9(F)(NH_3)$$

$$(\dot{T}) = (F)\left\{ k_8 \frac{(Cl^-)(NH_3)}{K_7(OH^-)} + k_9(NH_3) \right\}$$

Replacing (OH^-) by $K_{12}^{1/2}(NH_3)^{1/2}$ gives:

$$(\dot{T}) = \left\{ \frac{(T)}{1 + \dfrac{(Cl^-)}{K_7 K_{12}^{1/2}(NH_3)^{1/2}}} \right\} \left\{ \frac{k_8(Cl^-)(NH_3)^{1/2}}{K_7 K_{12}^{1/2}} + k_9(NH_3) \right\}$$

Of the four possible dominant terms, the single term of interest arises if

$$\frac{(Cl^-)}{K_7 K_{12}^{1/2}(NH_3)^{1/2}} \gg 1 \text{ and } k_9(NH_3) \gg \frac{k_8(Cl^-)(NH_3)^{1/2}}{K_7 K_{12}^{1/2}} .$$

The rate expression would then have the form:

$$(\dot{T}) \propto \frac{(T)(NH_3)^{3/2}}{(Cl^-)}$$

which corresponds to $Pd(NH_3)_3Cl^+$ being the dominant species in T and the step

$$Pd(NH_3)_3OH^+ + NH_3 \rightarrow Pd(NH_3)_4^{2+} + OH^-$$

being rate-controlling.

As far as the observations can be analyzed, the fast step (in 1.0$\underline{M}$ NaCl) can be identified with case (2) of the first ammonation step; and thus the slow step with the second ammonation, as analyzed above. A mechanism consistent with the observed rate constants of the fast step in 0.1$\underline{M}$ NaCl was not found.

A major area of possible analysis has been left unexamined: that of multiple term rate expressions, which may be indicated by the significant non-zero intercepts in figures 4,5,7,8. Additional investigation will be required to characterize fully the reaction of $\underline{cis}$-Pd(NH$_3$)Cl$_2$ with ammonia in an unbuffered medium, especially when chloride ion concentrations are less than 0.5$\underline{M}$ and temperature is varied.

The conclusions of this investigation may then be summarized as follows:

(1) It was not possible to confirm the form of the observed rate constant

$$k_{obs} = k_1 \frac{(NH_3)}{(Cl^-)} + k_2(NH_3)$$

as assumed by Atwill for the first and second ammonation reactions in neutral buffered medium. One reason for variation from Atwill's rate law is the relatively high concentration of ammonia utilized in this study. The hydrolysis of ammonia in an unbuffered solution leads to significant concentrations of hydroxide ion.

(2) Evidence was obtained of hydroxide-substituted species in a medium of pH 11.

(3) The identification of the first and second ammonation steps as the faster and slower observed steps, respectively, was inferred.

(4) A tentative rate law for the first (fast) ammonation step in 0.5$\underline{M}$ to 1.0$\underline{M}$ NaCl was found to be of the form

$$\text{rate} = k\frac{(NH_3)^2}{(Cl^-)} \left[Pd(NH_3)_2Cl(OH_2)^+ \right]$$

(5) A tentative form for the second (slow) ammonation step rate law in 0.1$\underline{M}$ to 1.0$\underline{M}$ NaCl was found to be

$$\text{rate} = k\frac{(NH_3)^{3/2}}{(Cl^-)} \left[Pd(NH_3)_3Cl^+ \right].$$

APPENDIX A - DATA FROM INDIVIDUAL KINETIC RUNS

Runs are identified using a seven character alphanumeric code. The first six characters are numerals indicating the date and the seventh a letter identifying the trace.

$[Cl^-] = 1.0\underline{M}$; $[NH_3] = 0.25\underline{M}$; $A_\infty = 0.0200$

$k_{fast} = 4.2$ sec^{-1}; $k_{slow} = 0.49$ sec^{-1}

TIME	ABSORBANCE
.000	.0773
.050	.0620
.100	.0477
.150	.0443
.200	.0419
.250	.0400
.300	.0391
.350	.0376
.400	.0367
.450	.0357
.500	.0353
.550	.0343
.600	.0339
.650	.0334
.700	.0329
.750	.0325
.800	.0320
.850	.0315
.900	.0310
1.000	.0310
1.200	.0292
1.400	.0280
1.600	.0273
1.800	.0269
2.000	.0262
2.500	.0250
3.000	.0235
3.500	.0230
4.000	.0223
5.000	.0216
6.000	.0219

RUN 740808B

$[Cl^-] = 1.0\underline{M}$; $[NH_3] = 0.25\underline{M}$; $\Lambda_\infty = 0.0218$

$k_{fast} = 3.4$ sec^{-1}; $k_{slow} = 0.50$ sec^{-1}

TIME	ABSORBANCE
.000	.0555
.050	.0521
.100	.5060
.150	.0494
.200	.0477
.250	.0465
.300	.0456
.350	.0446
.400	.0436
.450	.0429
.500	.0414
.550	.0405
.600	.0400
.650	.0398
.750	.0386
.850	.0374
1.000	.0360
1.200	.0348
1.400	.0334
1.600	.0325
1.800	.0315
2.000	.0306
3.000	.0273
4.000	.0258
5.000	.0246
6.000	.0235
7.000	.0232
8.000	.0227

RUN 740808C

$[Cl^-] = 1.0\underline{M}$; $[NH_3] = 0.25\underline{M}$; $A_\infty = 0.0216$

$k_{fast} = 4.8 \text{ sec}^{-1}$; $k_{slow} = 0.46 \text{ sec}^{-1}$

TIME	ABSORBANCE
.000	.0767
.050	.0706
.100	.0550
.150	.0491
.200	.0424
.250	.0419
.300	.0400
.350	.0391
.400	.0381
.450	.0369
.500	.0362
.550	.0355
.600	.0351
.700	.0346
.800	.0339
.900	.0329
1.000	.0323
1.200	.0308
1.400	.0301
1.600	.0287
1.800	.0280
2.000	.0273
3.000	.0258
4.000	.0237
5.000	.0232
6.000	.0227
7.000	.0223

RUN 740814A

$[Cl^-] = 1.0\underline{M}; \ [NH_3] = 0.05\underline{M}; \ A_\infty = 0.0119$

$k_{fast} = 0.55 \ sec^{-1}; \ k_{slow} = 0.052 \ sec^{-1}$

TIME	ABSORBANCE
.000	.0620
.500	.0487
1.000	.0456
1.500	.0429
2.000	.0412
2.500	.0398
3.000	.0381
3.500	.0369
4.000	.0360
4.500	.0353
5.000	.0351
6.000	.0341
7.000	.0329
8.000	.0325
13.000	.0260
15.000	.0250
17.000	.0232
20.000	.0214
22.000	.0209
25.000	.0200

RUN 740815A

$[Cl^-] = 1.0\underline{M}$; $[NH_3] = 0.05\underline{M}$; $A_\infty = 0.0186$

$k_{fast} = 0.68 \ sec^{-1}$; $k_{slow} = 0.18 \ sec^{-1}$

TIME	ABSORBANCE
1.000	.0757
1.500	.0615
2.000	.0535
3.000	.0424
4.000	.3510
5.000	.0306
6.000	.0282
7.000	.0260
8.000	.0246
9.000	.0229
10.000	.0223
12.000	.0214
14.000	.0204
16.000	.0200
18.000	.0195
20.000	.0193
25.000	.0191
30.000	.0189

RUN 740815B

$[Cl^-] = 1.0\underline{M}$; $[NH_3] = 0.05\underline{M}$; $A_\infty = 0.0188$

$k_{fast} = 0.39$ sec^{-1}; $k_{slow} = 0.034$ sec^{-1}

TIME	ABSORBANCE
.500	.0565
1.000	.0467
1.500	.0424
2.000	.0381
2.500	.0350
3.000	.0329
4.000	.0303
5.000	.0275
6.000	.0260
7.000	.0246
8.000	.0234
9.000	.0229
10.000	.0223
12.000	.0220
14.000	.0216
16.000	.0214
20.000	.0211

44

RUN 740815C

$[Cl^-] = 1.0\underline{M}$; $[NH_3] = 0.05\underline{M}$; $A_\infty = 0.0204$

$k_{fast} = 0.39$ sec^{-1}; $k_{slow} = 0.044$ sec^{-1}

TIME	ABSORBANCE
.500	.0530
1.000	.0458
1.500	.0429
2.000	.0386
2.500	.0353
3.000	.0329
4.000	.0306
5.000	.0287
6.000	.0273
7.000	.0260
8.000	.0252
9.000	.0246
10.000	.0237
12.000	.0234
14.000	.0229
16.000	.0225
18.000	.0223
25.000	.0220
30.000	.0216
35.000	.0214

44

RUN 740815D

$[Cl^-] = 1.0\underline{M}$; $[NH_3] = 0.05\underline{M}$; $A_\infty = 0.0204$

$k_{fast} = 0.43$ sec^{-1}; $k_{slow} = 0.070$ sec^{-1}

TIME	ABSORBANCE
.250	.0595
.500	.0545
.750	.0487
1.000	.0458
1.500	.0419
2.000	.0381
2.500	.0357
3.000	.0334
3.500	.0322
4.000	.0305
5.000	.0284
6.000	.0273
7.000	.0260
8.000	.0252
9.000	.0246
10.000	.0237
12.000	.0234
15.000	.0229
18.000	.0223
30.000	.0218

RUN 740815E

$[Cl^-] = 1.0\underline{M}$; $[NH_3] = 0.05\underline{M}$; $A_\infty = 0.0216$

$k_{fast} = 0.36$ sec^{-1}; $k_{slow} = 0.027$ sec^{-1}

TIME	ABSORBANCE
.050	.0942
.100	.0783
.150	.0711
.200	.0670
.250	.0635
.350	.0592
.500	.0555
.700	.0518
1.000	.0487
1.200	.0463
1.400	.0448
1.600	.0434
1.850	.0419
2.000	.0410
2.500	.0381
3.000	.0355
3.500	.0342
4.000	.0325
4.500	.0315
5.000	.0301
6.000	.0282
7.000	.0273
8.000	.0262
10.000	.0255
12.000	.0246
14.000	.0241
25.000	.0234
35.000	.0227

RUN 740815F

$[Cl^-] = 1.0\underline{M}$; $[NH_3] = 0.05\underline{M}$; $A_\infty = 0.0204$

$k_{fast} = 0.36 \text{ sec}^{-1}$; $k_{slow} = 0.014 \text{ sec}^{-1}$

TIME	ABSORBANCE
.250	.0580
.500	.0518
.750	.0477
1.000	.0453
1.500	.0412
2.000	.0381
2.500	.0357
3.000	.0339
3.500	.0320
4.000	.0310
4.500	.2960
5.000	.0287
6.000	.0273
7.000	.0264
8.000	.0257
10.000	.0243
12.000	.0237
15.000	.0233
20.000	.0232
25.000	.0229
35.000	.0225

RUN 740819A

$[Cl^-] = 1.0\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0150$

$k_{fast} = 0.51\ sec^{-1}$; $k_{slow} = 0.024\ sec^{-1}$

TIME	ABSORBANCE
.250	.1290
.500	.0640
.750	.0540
1.000	.0472
1.250	.0438
1.500	.0400
1.750	.0373
2.000	.0343
2.500	.0306
3.000	.0280
3.500	.0257
4.000	.0237
4.500	.0227
5.000	.0211
5.000	.0200
7.000	.0191
10.000	.0177
15.000	.0170
20.000	.0168
25.000	.0166
30.000	.0164

RUN 740819B

$[Cl^-] = 1.0\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0214$

$k_{fast} = 0.80$ sec^{-1}; $k_{slow} = 0.29$ sec^{-1}

TIME	ABSORBANCE
.150	.1180
.175	.1024
.200	.0894
.225	.0843
.250	.0794
.300	.0731
.350	.0690
.400	.0650
.450	.0630
.500	.0607
.550	.0590
.600	.0570
.700	.0545
.800	.0526
.900	.0506
1.000	.0487
1.200	.0467
1.400	.0438
1.600	.0419
1.800	.0397
2.000	.0381
2.500	.0345
3.000	.0320
3.500	.0298
4.500	.0271
5.500	.0255
6.500	.0241
7.500	.0235
8.500	.0229

RUN 740819C

$[Cl^-] = 1.0\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0223$

$k_{fast} = 0.80$ sec^{-1}; $k_{slow} = 0.17$ sec^{-1}

TIME	ABSORBANCE
.150	.1007
.200	.0853
.250	.0794
.300	.0747
.350	.0708
.400	.0685
.450	.0660
.500	.0640
.550	.0620
.500	.0605
.700	.0570
.800	.0550
.900	.0535
1.000	.0511
1.200	.0484
1.400	.0458
1.600	.0438
1.800	.0419
2.000	.0400
2.200	.0391
2.400	.0376
2.600	.0367
2.800	.0355
3.000	.0345
3.500	.0325
4.000	.0310
4.500	.0302
5.000	.0287
6.000	.0278
7.000	.0269
8.000	.0262
9.000	.0260
10.000	.0255
13.000	.0250

RUN 740819D

$[Cl^-] = 1.0\underline{M};\ [NH_3] = 0.125\underline{M};\ A_\infty = 0.0209$

$k_{fast} = 0.77\ sec^{-1};\ k_{slow} = 0.15\ sec^{-1}$

TIME	ABSORBANCE
.250	.1296
.275	.1209
.300	.1059
.325	.0867
.350	.0853
.375	.0815
.400	.0773
.425	.0744
.450	.0718
.500	.0687
.550	.0650
.600	.0630
.700	.0590
.800	.0560
.900	.0540
1.000	.0521
1.200	.0487
1.400	.0460
1.600	.0438
1.800	.0416
2.000	.0402
2.250	.0376
2.500	.0362
3.000	.0334
3.500	.0315
4.000	.0301
4.500	.0282
5.000	.0275
6.000	.0262
7.000	.0255
8.000	.0250
9.000	.0243
10.000	.0237
15.000	.0225

RUN 740918A

$[Cl^-] = 0.625\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0381$

$k_{fast} = 5.5$ sec^{-1}; $k_{slow} = 0.46$ sec^{-1}

TIME	ABSORBANCE
.050	.2341
.100	.1871
.150	.1498
.200	.1201
.250	.1154
.300	.1017
.350	.0924
.400	.0879
.500	.0835
.600	.0749
.700	.0706
1.000	.0663
1.300	.0622
1.800	.0580
2.200	.0538
2.800	.0498
3.600	.0458
4.400	.0417

RUN 740918B

$[Cl^-] = 0.625\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = .0458$

$k_{fast} = 8.0 \text{ sec}^{-1}$; $k_{slow} = 0.50 \text{ sec}^{-1}$

TIME	ABSORBANCE
.000	.2159
.050	.0173
.100	.1549
.150	.1273
.200	.1129
.250	.1015
.300	.0947
.400	.0879
.500	.0814
.600	.0769
.700	.0749
.800	.0725
1.000	.0706
1.500	.0642
2.000	.0621
2.500	.0580
3.000	.0559
3.400	.0538

RUN 740918C

$[Cl^-] = 0.625\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0458$

$k_{fast} = 7.4$ sec^{-1}; $k_{slow} = 0.52$ sec^{-1}

TIME	ABSORBANCE
.100	.1955
.150	.1446
.200	.1296
.300	.1035
.400	.0856
.500	.0814
.600	.0792
.700	.0735
.800	.0735
.900	.0706
1.000	.0684
1.200	.0663
1.400	.0642
1.700	.0621
2.000	.0605
2.600	.0559
3.000	.0538
3.400	.0518
3.700	.0497
4.000	.0477

RUN 740918D

$[Cl^-] = 0.625\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0497$

$k_{fast} = 5.7\ sec^{-1}$; $k_{slow} = 0.42\ sec^{-1}$

TIME	ABSORBANCE
.100	.2041
.150	.1565
.200	.1347
.250	.1177
.300	.1107
.350	.1015
.400	.0969
.450	.0901
.500	.0879
.600	.0835
.700	.0810
.800	.0790
.900	.0770
1.000	.0748
1.200	.0706
1.400	.0706
1.600	.0684
1.800	.0663
2.000	.0663
2.500	.0621
3.100	.0580
3.500	.0559
3.900	.0538

RUN 740918E

$[Cl^-] = 0.625\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0518$

$k_{fast} = 6.3 \text{ sec}^{-1}$; $k_{slow} = 0.48 \text{ sec}^{-1}$

TIME	ABSORBANCE
.000	.2188
.050	.1899
.100	.1601
.150	.1322
.200	.1177
.250	.1107
.300	.0992
.400	.0924
.500	.0857
.600	.0835
.700	.0810
.800	.0770
.900	.0770
1.000	.0748
1.200	.0727
1.400	.0706
1.600	.0684
1.800	.0663
2.000	.0663
2.500	.0621
3.100	.0600
3.500	.0559

RUN 740918F

$[Cl^-] = 0.625\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0538$

$k_{fast} = 7.1\ sec^{-1}$; $k_{slow} = 0.56\ sec^{-1}$

TIME	ABSORBANCE
.000	.2280
.050	.1899
.100	.1575
.150	.1322
.200	.1177
.250	.1107
.300	.1037
.400	.0924
.500	.0879
.600	.0856
.700	.0814
.800	.0792
.900	.0792
1.000	.0770
1.200	.0727
1.400	.0727
1.600	.0706
1.800	.0684
2.000	.0684
2.200	.0663
2.400	.0642
2.700	.0621
3.100	.0600
3.500	.0580

$[Cl^-] = 0.625\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0518$

$k_{fast} = 7.0$ sec^{-1}; $k_{slow} = N \cdot A \cdot$

TIME	ABSORBANCE
.000	.2372
.020	.2188
.040	.2041
.060	.1871
.080	.1734
.100	.1601
.140	.1422
.180	.1273
.220	.1177
.260	.1107
.300	.1037
.380	.0969
.460	.0924
.560	.0879
.700	.0835
.820	.0814
.940	.0770
1.000	.0770

RUN 740919A

$[Cl^-] = 0.5\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0458$

$k_{fast} = 11 \ sec^{-1}$; $k_{slow} = 1.3 \ sec^{-1}$

TIME	ABSORBANCE
.040	.2188
.060	.1984
.080	.1898
.100	.1680
.120	.1549
.140	.1422
.160	.1347
.180	.1249
.200	.1154
.240	.1061
.280	.0969
.320	.0902
.360	.0857
.400	.0813
.480	.0770
.560	.0727
.680	.0684
.840	.0664
1.000	.0621
1.320	.0621
1.400	.0559
1.600	.0539
1.800	.0518

RUN 740919B

$[Cl^-] = 0.5\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0458$

$k_{fast} = 8.8 \ sec^{-1}$; $k_{slow} = 1.1 \ sec^{-1}$

TIME	ABSORBANCE
.020	.2099
.040	.1955
.060	.1734
.080	.1654
.100	.1447
.140	.1273
.180	.1130
.240	.0946
.320	.0857
.400	.0770
.480	.0727
.560	.0706
.680	.0664
.840	.0642
1.000	.0621
1.240	.0580
1.600	.0539
2.000	.0498

RUN 740919C

$[Cl^-] = 0.5\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0458$

$k_{fast} = 8.8 \ sec^{-1}$; $k_{slow} = 0.96 \ sec^{-1}$

TIME	ABSORBANCE
.020	.2188
.040	.2070
.060	.1871
.080	.1707
.100	.1549
.120	.1447
.140	.1347
.160	.1273
.180	.1154
.200	.1107
.240	.1015
.280	.0946
.320	.0879
.360	.0835
.400	.0813
.480	.0749
.560	.0727
.680	.0684
.840	.0664
1.000	.0642
1.240	.0600
1.400	.0580
1.800	.0539
2.000	.0498

$[Cl^-] = 0.5\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0458$

$k_{fast} = 9.1$ sec^{-1}; $k_{slow} = 0.88$ sec^{-1}

TIME	ABSORBANCE
.020	.0637
.040	.0619
.060	.1843
.080	.1680
.100	.1574
.120	.1422
.140	.1322
.160	.1249
.180	.1163
.200	.1083
.240	.0992
.280	.0946
.320	.0902
.400	.0813
.520	.0770
.600	.0727
.760	.0706
.920	.0664
1.080	.0621
1.240	.0600
1.600	.0580
2.000	.0518

RUN 740919E

$[Cl^-] = 0.5\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0458$

$k_{fast} = 8.9$ sec^{-1}; $k_{slow} = 0.88$ sec^{-1}

TIME	ABSORBANCE
.000	.2310
.020	.2188
.040	.2099
.060	.1788
.080	.1680
.100	.1523
.120	.1447
.140	.1347
.160	.1273
.180	.1178
.200	.1107
.280	.0969
.360	.0857
.440	.0813
.520	.0770
.600	.0727
.760	.0706
.920	.0684
1.000	.0664
1.320	.0621
1.600	.0580
2.000	.0539

$[Cl^-] = 0.1\underline{M}; [NH_3] = 0.125\underline{M}; A_\infty = 0.0280$

$k_{fast} = 5.5 \ sec^{-1}; k_{slow} = 0.30 \ sec^{-1}$

TIME	ABSORBANCE
.020	:1761
.040	.1600
.060	.1471
.080	.1371
.100	.1272
.120	.1201
.140	.1129
.160	.1083
.180	.1014
.200	.0991
.240	.0901
.280	.0856
.320	.0813
.400	.0748
.480	.0705
.560	.0663
.700	.0642
.900	.0600
1.200	.0579
1.600	.0538
2.000	.0518

RUN 740923B

$[Cl^-] = 0.1\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0280$

$k_{fast} = 7.2$ sec^{-1}; $k_{slow} = 0.40$ sec^{-1}

TIME	ABSORBANCE
.020	.1815
.040	.1653
.060	.1522
.080	.1396
.100	.1322
.120	.1224
.140	.1177
.160	.1106
.180	.1060
.200	.1014
.240	.0923
.280	.0879
.320	.0813
.360	.0791
.440	.0727
.520	.0684
.600	.0663
.800	.0642
1.000	.0600
1.400	.0558
1.800	.0538

RUN 740923C

$[Cl^-] = 0.1\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0280$

$k_{fast} = 6.8 \text{ sec}^{-1}$; $k_{slow} = 0.35 \text{ sec}^{-1}$

TIME	ABSORBANCE
.020	.1815
.040	.1600
.060	.1497
.080	.1396
.100	.1272
.120	.1177
.140	.1129
.160	.1060
.180	.1037
.200	.0991
.240	.0901
.280	.0835
.320	.0813
.360	.0769
.440	.0705
.520	.0663
.600	.0642
.760	.0621
.920	.0579
1.300	.0558
1.800	.0518

RUN 740923D

$[Cl^-] = 0.1\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0280$

$k_{fast} = 7.8$ sec^{-1}; $k_{slow} = 0.50$ sec^{-1}

TIME	ABSORBANCE
.020	.1679
.040	.1574
.060	.1446
.080	.1322
.100	.1249
.120	.1177
.140	.1129
.160	.1060
.180	.1014
.200	.0968
.240	.0901
.280	.0856
.320	.0791
.380	.0769
.440	.0727
.520	.0684
.600	.0662
.680	.0642
.800	.0621
.960	.0600
1.200	.0579

RUN 740923E

$[Cl^-] = 0.1\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0280$

$k_{fast} = 6.8$ sec^{-1}; $k_{slow} = 0.30$ sec^{-1}

TIME	ABSORBANCE
.020	.1787
.040	.1601
.060	.1497
.080	.1346
.100	.1297
.120	.1201
.140	.1153
.160	.1083
.180	.1014
.200	.0991
.240	.0923
.280	.0879
.320	.0835
.360	.0791
.400	.0748
.560	.0684
.720	.0663
.900	.0642
1.200	.0600
1.600	.0579
2.000	.0558

RUN 740923F

$[Cl^-] = 0.1\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0280$

$k_{fast} = 7.0 \text{ sec}^{-1}$; $k_{slow} = 0.35 \text{ sec}^{-1}$

TIME	ABSORBANCE
.010	.1787
.020	.1679
.030	.1626
.040	.1574
.050	.1522
.060	.1446
.080	.1346
.100	.1272
.120	.1201
.140	.1129
.160	.1060
.180	.1014
.200	.0968
.240	.0923
.320	.0835
.480	.0727
.620	.0663
.840	.0621
1.000	.0600

$[Cl^-] = 0.1\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0280$

$k_{fast} = 7.1 \ sec^{-1}$; $k_{slow} = 0.35 \ sec^{-1}$

TIME	ABSORBANCE
.010	.1679
.020	.1600
.030	.1548
.040	.1497
.050	.1446
.070	.1297
.090	.1249
.110	.1177
.130	.1106
.150	.1060
.170	.1014
.190	.0968
.210	.0946
.240	.0901
.280	.0835
.340	.0791
.460	.0727
.600	.0684
.720	.0642
1.000	.0600

$[Cl^-] = 0.1\underline{M}$; $[NH_3] = 0.125\underline{M}$; $A_\infty = 0.0280$

$k_{fast} = 7.0 \text{ sec}^{-1}$; $k_{slow} = 0.36 \text{ sec}^{-1}$

TIME	ABSORBANCE
.010	.1815
.020	.1733
.030	.1679
.040	.1600
.050	.1548
.060	.1471
.070	.1421
.090	.1346
.110	.0976
.130	.1177
.150	.1106
.170	.1060
.190	.1014
.250	.0902
.380	.0791
.460	.0727
.560	.0705
.700	.0663
.800	.0621
1.000	.0600

RUN 741012A

$[Cl^-] = 0.1\underline{M}$; $[NH_3] = 0.05\underline{M}$; $A_\infty = 0.0538$

$k_{fast} = 4.7 \text{ sec}^{-1}$; $k_{slow} = 0.22 \text{ sec}^{-1}$

TIME	ABSORBANCE
.200	.2068
.250	.1814
.300	.1652
.350	.1471
.400	.1420
.450	.1321
.500	.1272
.600	.1176
.700	.1129
.800	.1082
.900	.1059
1.000	.1036
1.200	.0991
1.400	.0968
1.600	.0945
1.800	.0945
2.000	.0900
2.600	.0856
3.400	.0812
4.100	.0769
4.500	.0748

$[Cl^-] = 0.1\underline{M}$; $[NH_3] = 0.05\underline{M}$; $A_\infty = 0.0538$

$k_{fast} = 5.0$ sec^{-1}; $k_{slow} = 0.23$ sec^{-1}

TIME	ABSORBANCE
.250	.2278
.300	.2011
.350	.1841
.400	.1548
.450	.1471
.500	.1395
.550	.1321
.600	.1248
.700	.1152
.800	.1106
.900	.1059
1.000	.1036
1.200	.0991
1.400	.0968
1.600	.0923
2.000	.0900
2.600	.0856
3.200	.0812
4.000	.0769
4.500	.0726

RUN 741012C

$[Cl^-] = 0.1\underline{M}$; $[NH_3] = 0.05\underline{M}$; $A_\infty = 0.0538$

$k_{fast} = 5.4\ sec^{-1}$; $k_{slow} = 0.22\ sec^{-1}$

TIME	ABSORBANCE
.100	.2309
.150	.2011
.200	.1787
.250	.1626
.300	.1522
.350	.1420
.400	.1346
.450	.1321
.500	.1272
.550	.1200
.600	.1152
.700	.1129
.800	.1106
.900	.1059
1.000	.1036
1.200	.1014
1.400	.0991
1.600	.0991
1.800	.0968
2.000	.0945
2.400	.0900
2.800	.0878
3.400	.0856
3.800	.0834
4.500	.0769

RUN 741012D

$[Cl^-] = 0.1\underline{M}$; $[NH_3] = 0.05\underline{M}$; $A_\infty = 0.0538$

$k_{fast} = 5.5 \text{ sec}^{-1}$; $k_{slow} = 0.19 \text{ sec}^{-1}$

TIME	ABSORBANCE
.100	.2370
.150	.2098
.200	.1841
.250	.1652
.300	.1522
.350	.1446
.400	.1370
.450	.1296
.500	.1272
.600	.1176
.700	.1152
.800	.1082
.900	.1059
1.000	.1059
1.200	.1014
1.400	.1014
1.600	.0991
1.800	.0968
2.000	.0945
2.400	.0900
3.000	.0878
3.800	.0834
4.500	.0769

RUN 741012E

$[Cl^-] = 0.1\underline{M}$; $[NH_3] = 0.05\underline{M}$; $A_\infty = 0.0538$

$k_{fast} = 4.5$ sec^{-1}; $k_{slow} = 0.15$ sec^{-1}

TIME	ABSORBANCE
.050	.2157
.100	.2040
.150	.1869
.200	.1652
.250	.1548
.300	.1420
.350	.1370
.400	.1321
.450	.1272
.500	.1248
.600	.1176
.700	.1152
.800	.1106
.900	.1082
1.000	.1082
1.200	.1036
1.400	.1014
1.600	.1014
2.000	.0991
2.600	.0945
3.400	.0878
4.100	.0856
4.500	.0812

$[Cl^-] = 0.1\underline{M}$; $[NH_3] = 0.25\underline{M}$; $A_\infty = 0.0091$

$k_{fast} = 9.2 \ sec^{-1}$; $k_{slow} = 0.72 \ sec^{-1}$

TIME	ABSORBANCE
.040	.1815
.050	.1733
.060	.1653
.070	.1548
.080	.1446
.090	.1371
.100	.1297
.110	.1201
.120	.1153
.130	.1106
.140	.1060
.150	.1037
.170	.0946
.190	.0879
.220	.0791
.260	.0727
.300	.0663
.380	.0579
.460	.0518
.580	.0457
.720	.0417
.860	.0397
1.000	.0397

RUN 741013B

$[Cl^-] = 0.1\underline{M}$; $[NH_3] = 0.25\underline{M}$; $A_\infty = 0.0091$

$k_{fast} = 12\ sec^{-1}$; $k_{slow} = 1.1\ sec^{-1}$

TIME	ABSORBANCE
.040	.1733
.050	.1653
.060	.1548
.070	.1471
.080	.1346
.090	.1297
.100	.1201
.110	.1129
.120	.1060
.130	.1014
.140	.0968
.150	.0923
.170	.0856
.190	.0791
.220	.0705
.260	.0621
.300	.0579
.380	.0518
.460	.0477
.580	.0437
.740	.0377
.820	.0358

RUN 741013C

$[Cl^-] = 0.1\underline{M}$; $[NH_3] = 0.25\underline{M}$; $A_\infty = 0.0091$

$k_{fast} = 10 \ sec^{-1}$; $k_{slow} = 0.76 \ sec^{-1}$

TIME	ABSORBANCE
.040	.1761
.050	.1653
.060	.1574
.070	.1471
.080	.1371
.090	.1322
.100	.1201
.110	.1153
.120	.1106
.140	.1014
.160	.0923
.180	.0835
.200	.0791
.240	.0705
.280	.0621
.340	.0579
.420	.0518
.500	.0457
.660	.0417
.820	.0377
1.000	.0358

RUN 741013D

$[Cl^-] = 0.1\underline{M}$; $[NH_3] = 0.25\underline{M}$; $A_\infty = 0.0091$

$k_{fast} = 9.8\ sec^{-1}$; $k_{slow} = 0.71\ sec^{-1}$

TIME	ABSORBANCE
.040	.1706
.050	.1600
.060	.1548
.070	.1471
.080	.1396
.090	.1297
.100	.1224
.110	.1201
.120	.1129
.130	.1106
.140	.1037
.150	.0991
.170	.0946
.190	.0879
.220	.0791
.260	.0727
.300	.0684
.380	.0579
.460	.0558
.580	.0497
.740	.0457
.900	.0417
1.000	.0417

RUN 741013E

$[Cl^-] = 0.1\underline{M}$; $[NH_3] = 0.25\underline{M}$; $A_\infty = 0.0091$

$k_{fast} = 9.6 \text{ sec}^{-1}$; $k_{slow} = 0.44 \text{ sec}^{-1}$

TIME	ABSORBANCE
.060	.1456
.070	.1386
.080	.1278
.090	.1210
.100	.1172
.110	.1078
.120	.1053
.130	.1005
.140	.0959
.150	.0897
.170	.0852
.190	.0782
.220	.0714
.260	.0663
.300	.0621
.380	.0554
.460	.0505
.580	.0465
.740	.0433
.900	.0409
1.000	.0401

RUN 741014A

$[Cl^-] = 0.1\underline{M}$; $[NH_3] = 0.025\underline{M}$; $A_\infty = 0.0110$

$k_{fast} = 3.4$ sec^{-1}; $k_{slow} = 0.14$ sec^{-1}

TIME	ABSORBANCE
.100	.1983
.150	.1815
.200	.1574
.250	.1391
.300	.1273
.350	.1201
.400	.1060
.500	.0992
.600	.0901
.700	.0857
.800	.0792
.900	.0770
1.000	.0748
1.200	.0727
1.400	.0684
1.600	.0663
1.800	.0663
2.000	.0642
2.400	.0600
2.800	.0579
3.300	.0559
3.900	.0518
4.500	.0477
5.000	.0437

RUN 741014B

$[Cl^-] = 0.1\underline{M}$; $[NH_3] = 0.025\underline{M}$; $A_\infty = 0.0110$

$k_{fast} = 3.6 \ sec^{-1}$; $k_{slow} = 0.15 \ sec^{-1}$

TIME	ABSORBANCE
.100	.2099
.150	.1870
.200	.1627
.250	.1472
.300	.1322
.350	.1249
.400	.1153
.450	.1107
.500	.1060
.600	.0969
.700	.0901 ·
.800	.0857
.900	.0835
1.000	.0813
1.200	.0770
1.400	.0748
1.600	.0727
1.800	.0705
2.000	.0684
2.400	.0642
2.800	.0621
3.300	.0579
3.900	.0538
4.500	.0518
5.000	.0497

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